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NEW ARYLOXY ALKOXYSILANES (D) (U)

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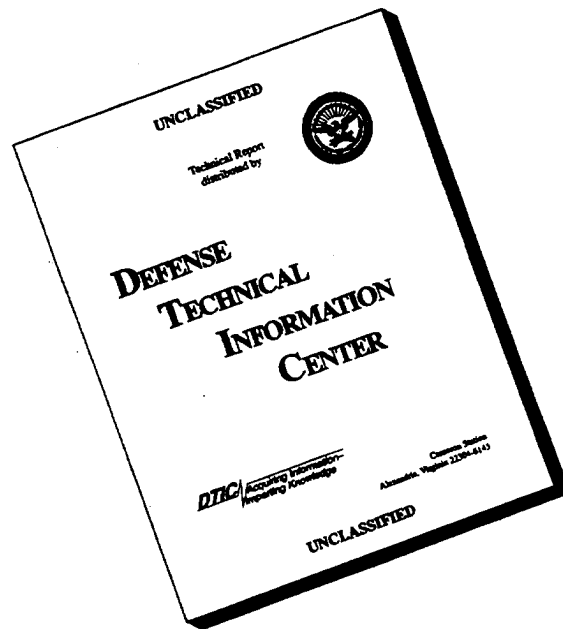
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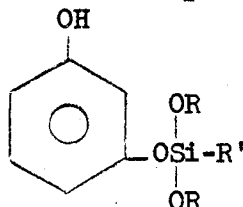
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NEW ARYLOXY ALKOXYSILANES (I) (U)

Prepared by:
James V. Duffy
Porter W. Erickson

ABSTRACT: A total of ten new aryloxy alkoxysilanes have been synthesized that are potential glass fiber finish chemicals for several resin systems. The generalized structure for these compounds is:



The R group is usually either methyl or ethyl while R' can be epoxy, amine, alcohol, ester or olefin. These aryloxy silanes were prepared by the partial condensation reaction between resorcinol and the following silanes: β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, δ -glycidoxypropyltrimethoxysilane, N,N bis(β -hydroxyethyl)- δ -aminopropyltriethoxysilane, γ -aminopropyltriethoxysilane, β -carbethoxyethyltriethoxysilane, vinyltriethoxysilane, vinyl-tris(β -methoxyethoxy)silane, δ -methacryloxypropyltrimethoxysilane, 3-cyclohexenetriethoxysilane and allyltriethoxysilane.

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CHEMISTRY RESEARCH DEPARTMENT
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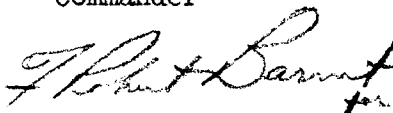
NEW ARYLOXY ALKOXYSILANES (I)

A series of new alkoxy derivatives of NOL-24 (U. S. Patent 2,720,470) have been synthesized and are discussed in this report. These glass finishes in addition to being more stable compounds than NOL-24 also contain various new reactive functional groups.

These compounds have not been isolated to date due to their reactive nature. Consequently, their structural formulae have not been determined but are assumed, based on the types of reactions expected due to their similarity to other known chemical reactions.

This is part of the work performed under POLARIS Research Task PR-4.

R. E. ODENING
Captain, USN
Commander



ALBERT LIGHTBODY
By direction

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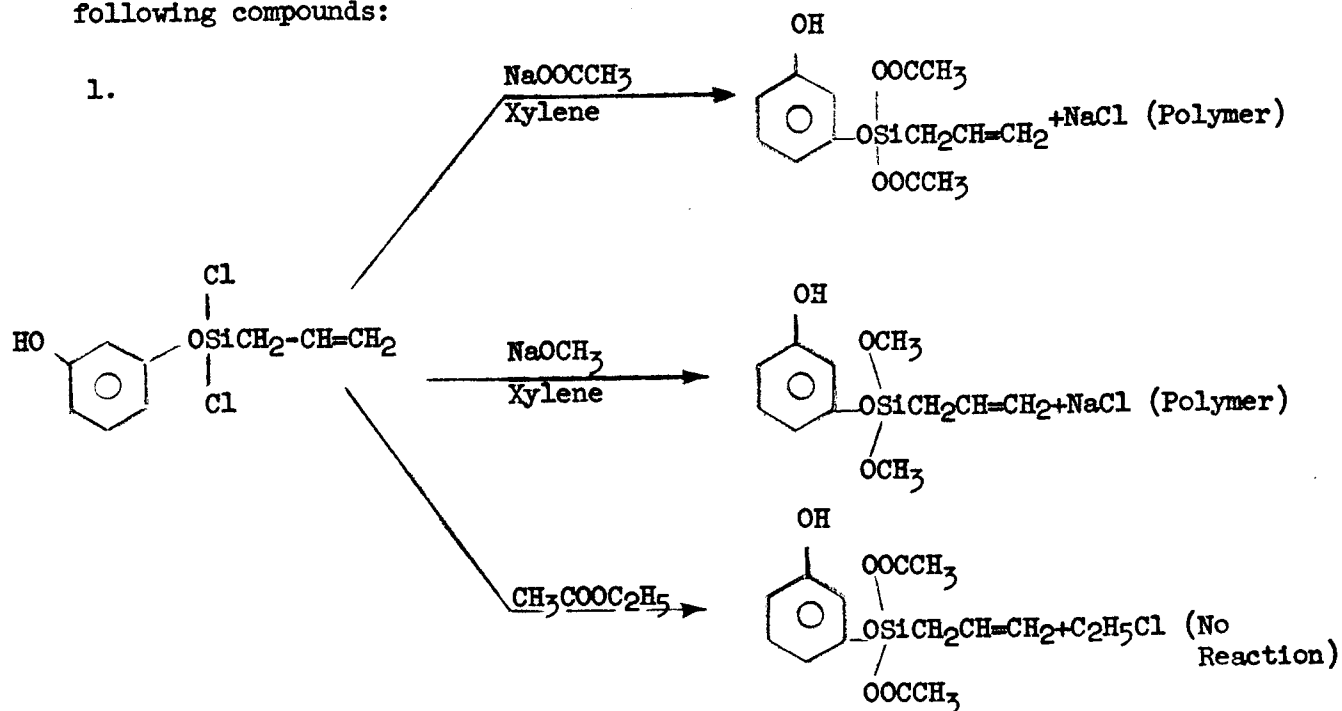
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- (g) Shechter, L., and Wynstra, J., Ind. and Eng. Chem., 48, No. 1, 86, (1956)
- (h) Boyd, D. R., and Marle, E. R., J. Chem. Soc., 105, 2117 (1914)
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INTRODUCTION

Chemical finishes are widely used to improve the strength properties of glass fiber plastic composites. These finishing materials can be divided into three general classes of compounds: alkoxysilanes, chrome complexes and chlorosilanes. NOL-24 is an aryloxy chlorosilane which was first prepared at these laboratories by Erickson in 1955 (ref. (a)). This material is an excellent glass fiber finish for epoxy, phenolic, melamine and polyester glass reinforced composites and provides retention of strength after severe exposure to moist environments. Flexural strengths as high as 150,000 psi have been reported for epoxy laminates containing NOL-24 finished glass cloth (Style 181) with usual wet strength retentions up to 95 percent (ref. (b)). In spite of its superior performance in reinforced plastics, NOL-24 is commercially impractical because of its susceptibility to hydrolysis by moisture. Furthermore, it requires the use of flammable solvents and produces a corrosive by-product (hydrogen chloride) which further limit its usefulness.

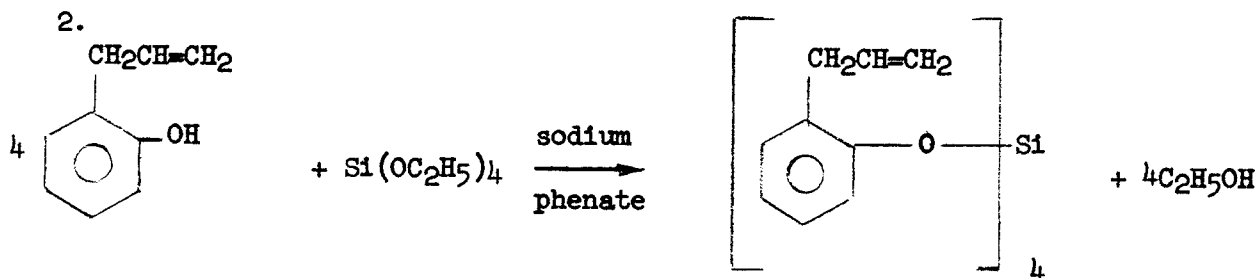
In an effort to increase the practicality of NOL-24 as a glass finish, attempts have been made to modify the structure in such a way as to eliminate the inherent disadvantages without affecting its excellent finish properties. Initially, the approach taken was to convert the existing chlorosilane finish to the more stable and less corrosive alkoxysilane or ester derivative. Reactions with sodium acetate, sodium methylate and ethyl acetate were studied in an effort to prepare the following compounds:



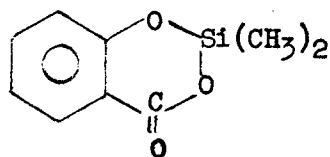
This indirect approach proved to be infeasible but led to a direct preparative route to the desired compounds. This report discusses ten new aryloxy alkoxy silanes which have been synthesized during the course of this investigation. All of these new materials are structural derivatives of NOL-24 and in addition possess increased stability and resistance to hydrolysis. The finish properties of these compounds are being evaluated and will be discussed in a subsequent report.

HISTORICAL

It has been known for sometime that alkoxy silanes transesterify with aliphatic alcohols and this reaction has been used as a convenient method for synthesizing higher tetraalkoxy silanes (ref. (c)). Malatesta (ref. (d)) in 1948 suggested the possibility of transesterifying tetraethyl ortho-silicate with phenol in the presence of aluminum or sodium ethylate. However, it was not until 1956 that Voronkov and Karpenko (ref. (e)) used this reaction in the preparation of tetraaryloxy silanes about which they stated "in contrast to alkoxy silanes - aryloxy silanes are hardly mentioned in the literature". A typical reaction involved the preparation of tetra(o-allylphenoxy) silane:

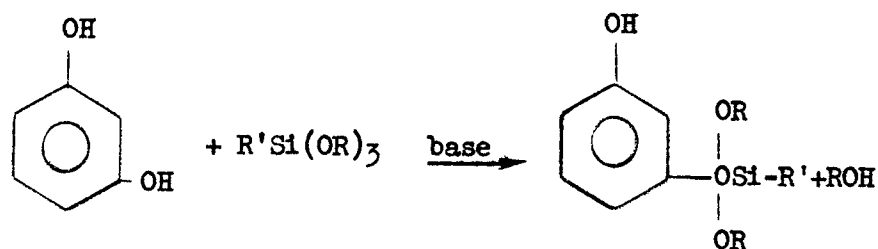


In a more recent work, Mehrotra and Pant (ref. (f)) showed that dimethyldiethoxysilane will react with salicylic acid to form the cyclic product



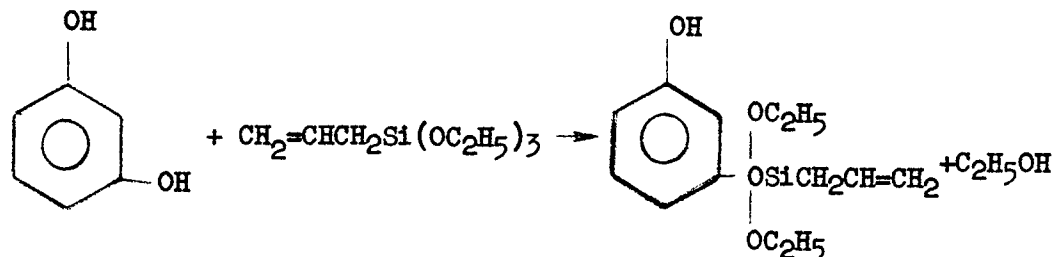
All of this previous work led us to believe that resorcinol would react with various commercially available alkoxy silanes to yield new NOL-24 derived finishes. A general mechanism for this reaction can be written as follows:

3.



The R group generally represents methyl or ethyl while R' can be any organic moiety containing reactive functional groups. Indeed this method was used to prepare directly the alkoxy derivative of NOL-24:

4.

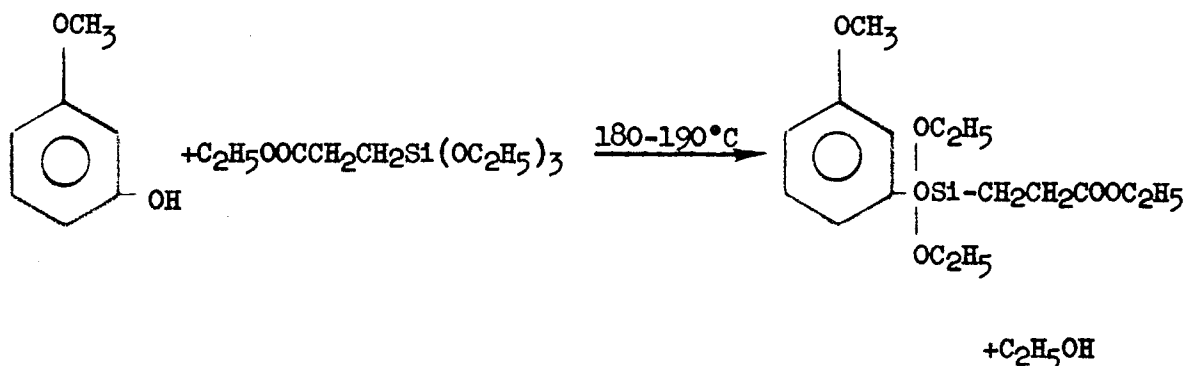


EXPERIMENTAL WORK AND RESULTS

The details of the procedure and materials used are shown in Appendix A and B respectively.

A model reaction involving a resorcinol derivative (m-methoxyphenol) and an alkoxy silane was studied initially to determine the feasibility of this approach. The reaction between m-methoxyphenol and β -carbethoxyethyltriethoxysilane was carried to 93% completion to yield the following product:

5.



This particular phenol was selected because the product did not contain residual hydroxyl and could be purified by distillation without further polymerization. Fractional distillation at a temperature of 166-168°C/0.45 mm yielded a compound having the following carbon-hydrogen analysis:

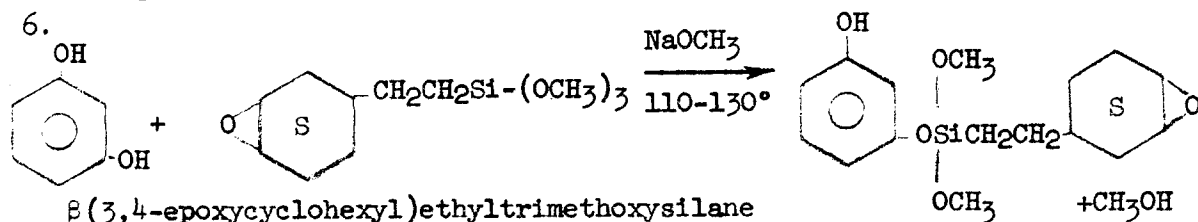
	<u>Theoretical</u>	<u>Found</u>
Carbon	56.12	56.04
Hydrogen	7.65	7.24

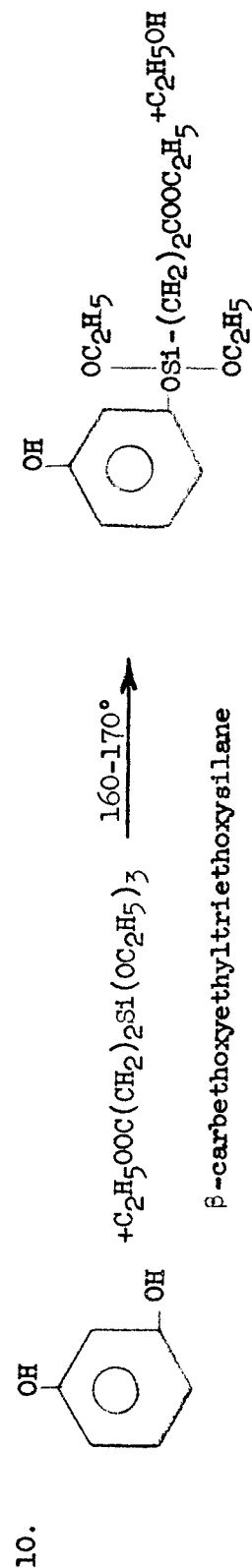
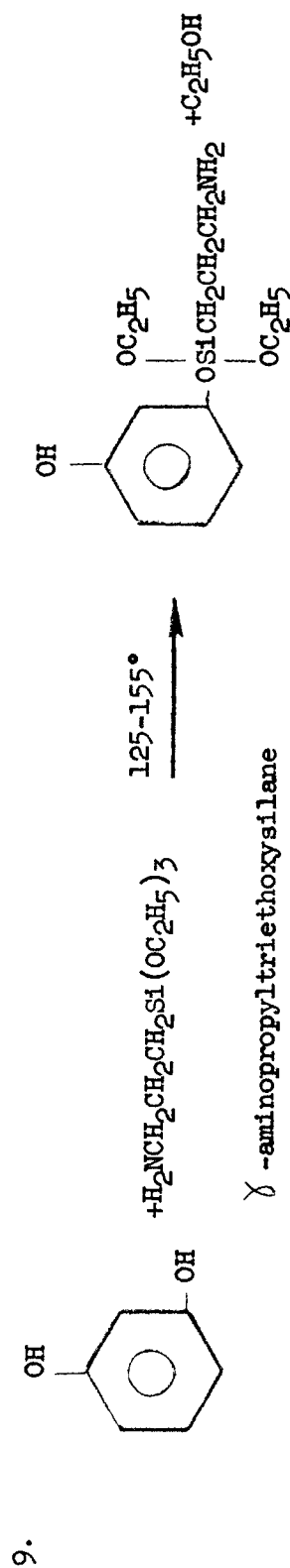
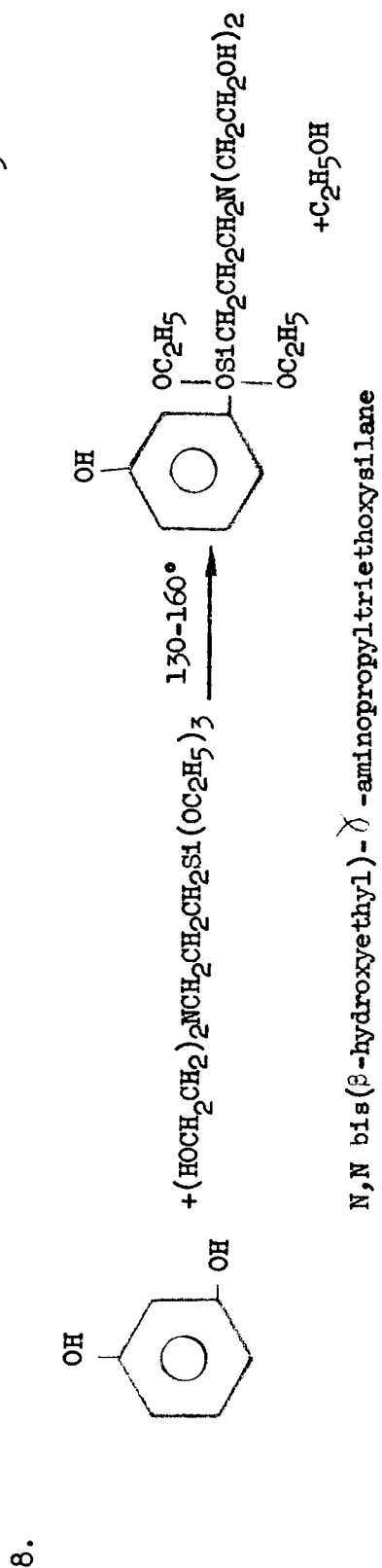
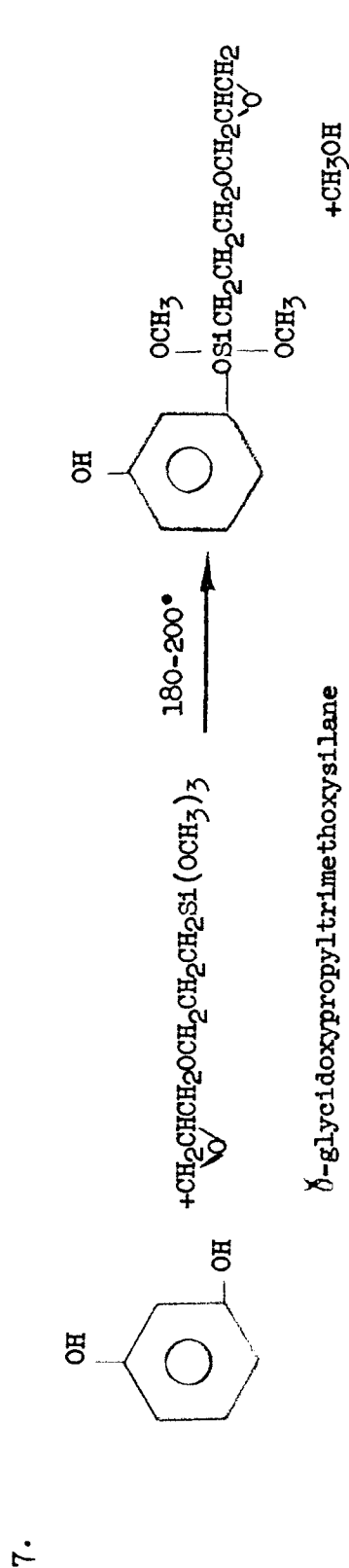
The infra-red spectra (Fig. 1) of the initial and final reaction mixtures show loss of absorption at 3400 cm^{-1} which corresponds to phenolic hydroxyl. The spectra further show decreased $-\text{CH}_2-$ absorption in the region of 3000-2800 cm^{-1} and below 1500 cm^{-1} due to the loss of ethanol from the reaction mixture. The retention of the doublet at 1725 cm^{-1} can be attributed to the carbethoxy group which does not take part in the reaction. These results show that the condensation reaction takes place between the phenolic hydroxyl and ethoxy silane group.

This model reaction is used as the basis for writing structures for the products obtained from other resorcinol-alkoxysilane reactions. However, in the case of these materials, we are dealing with reactive intermediates which can undergo further reaction leading to polymer formation. The presence of residual hydroxyl in these reaction products is confirmed by the strong infra-red absorption in the region of 3400 cm^{-1} . These hydroxyl groups cause the compounds to have very high boiling points even at high vacuums. The result of these factors is that the reaction temperature is reached before the compound boils and polymerization occurs.

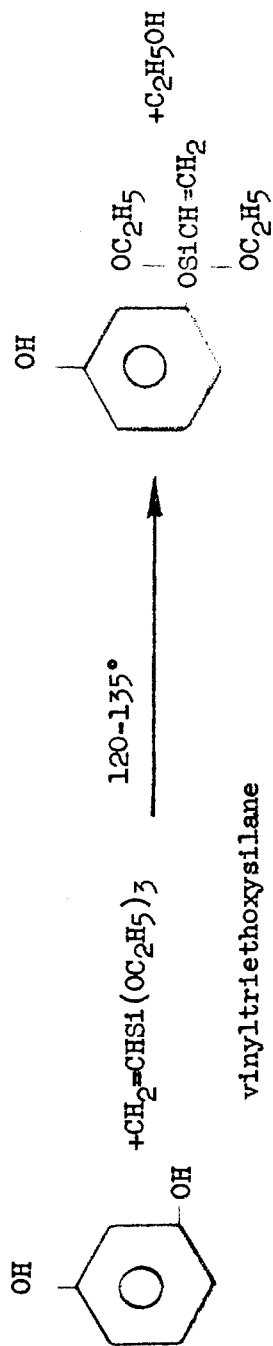
The capability of obtaining high vacuum has been now realized and further attempts at isolation of these compounds by fractional distillation will be made. Another possible approach to this problem of separation is to use a blocking group such as $-\text{Si}(\text{CH}_3)_3$ to inactivate the phenolic hydroxyl. This compound could be distilled and then by selective hydrolysis it might be possible to obtain the desired material.

In view of the existing difficulties the materials which have been prepared have not yet been isolated as pure compounds. It is felt, however, that since the reaction is a simple condensation (see Discussion) the products obtained in most cases should be sufficiently pure to permit their evaluation as glass finishes. The compounds prepared include the following:

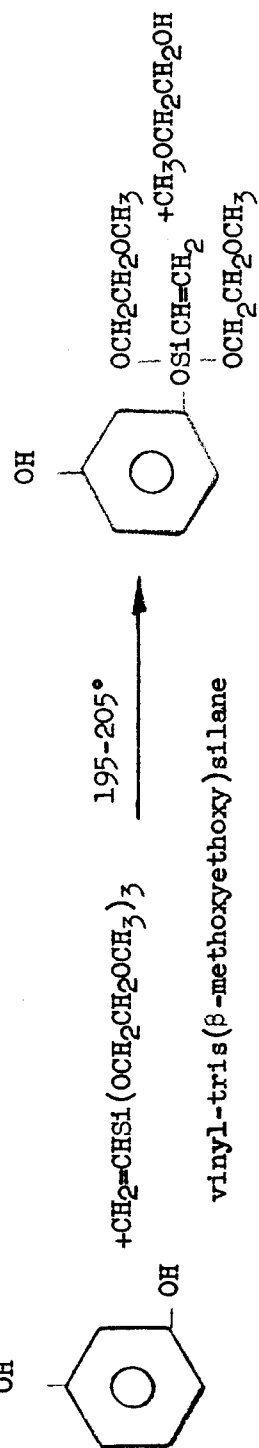




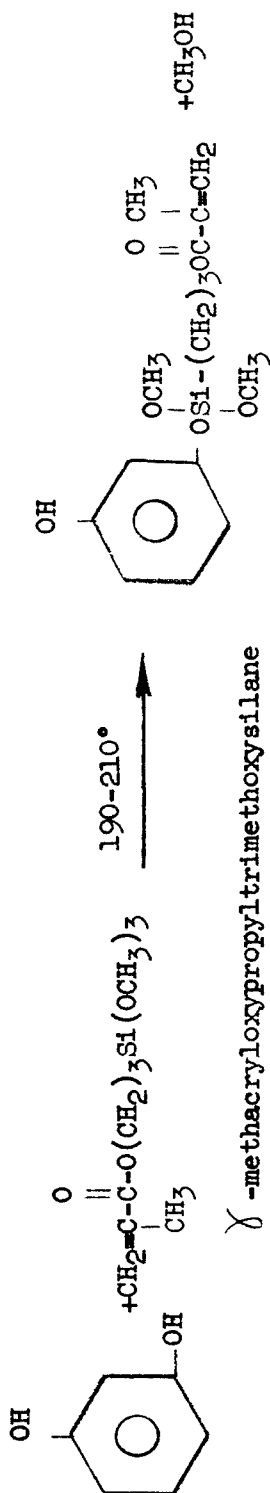
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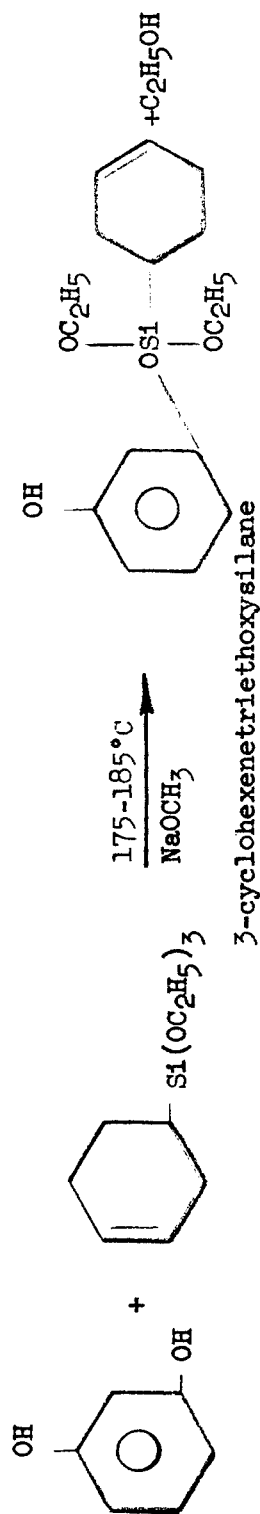
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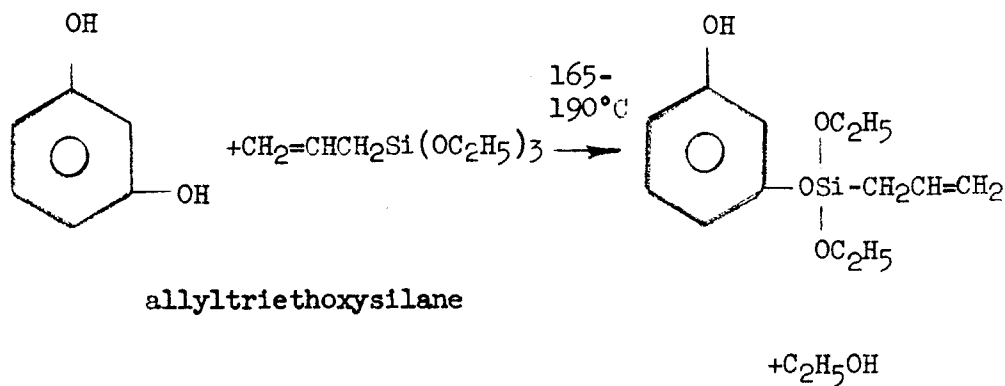
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14.



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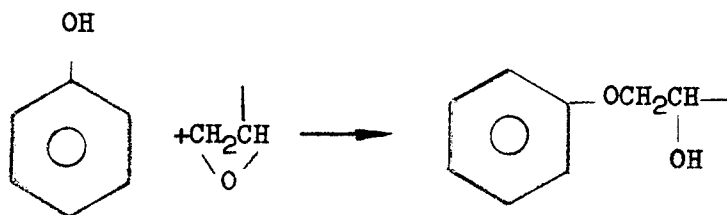


DISCUSSION OF POSSIBLE SIDE REACTIONS

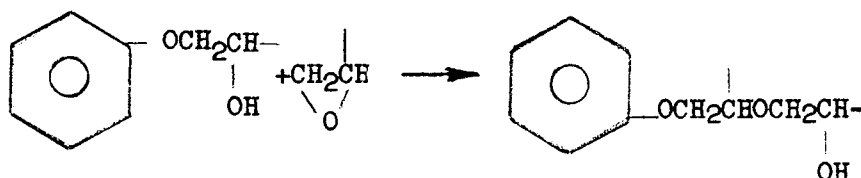
Single reaction products have been written in each case which is perhaps an oversimplification of the actual situation. It is advisable, therefore, to review some of the possible side reactions which can occur during the preparation of several of these materials.

Shechter and Wynstra (ref. (g)) have shown that two types of reaction are possible between phenol and glycidyl ether. The initial reaction is that of the phenolic hydroxyl with epoxide and the subsequent reaction of the aliphatic alcohol generated in the first reaction with epoxide. These reactions can be written as follows:

16.

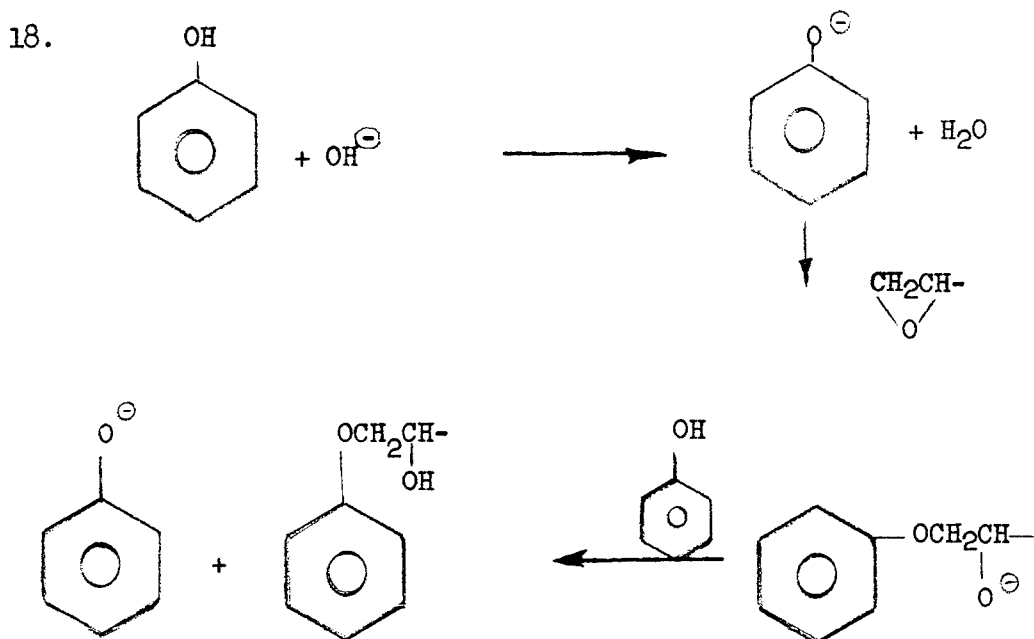


17.



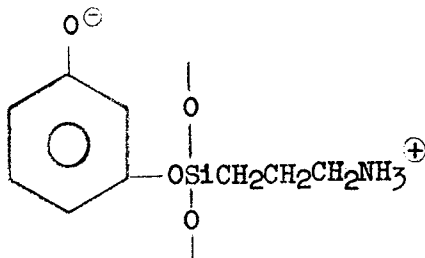
Noncatalyzed at 200°C the rate of the second reaction was more rapid than that of phenolic hydroxyl with epoxide. This is quite significant

when one realizes that the initial aliphatic hydroxyl concentration was zero and became finite only after some epoxide reacted with phenol. It was concluded that the phenol acted as a catalyst for the second reaction. The base catalyzed reaction of phenol with glycidyl ether proceeded at a lower temperature to the exclusion of any alcohol-epoxide reaction. A mechanism for this reaction was proposed by Boyd and Marle (ref. (h)) and Patat, Cremer and Bobleter (ref. (i)). This mechanism can be represented as follows:



By analogy, one could write similar reactions between resorcinol and epoxysilanes (reactions 6 and 7) and predict similar side product formation. The side reactions in this case would be in direct competition with the phenolic hydroxyl alkoxysilane reaction. A further complication is the fact that both reactions are base catalyzed. Our work shows qualitatively that at 110-120°C the sodium methylate catalyzed reaction of resorcinol and γ -glycidoxypropyltrimethoxysilane (reaction 7) produced a polymeric gel while the same reaction at 180-200°C without catalyst yielded a liquid product. It appears that the catalyzed reaction at lower temperatures favored more of the resorcinol-epoxide reaction than the noncatalyzed reaction at higher temperatures. In the reaction of resorcinol with β (3,4-epoxycyclohexyl)ethyltrimethoxysilane (reaction 6), polymerization occurred at 180°C without catalyst while a liquid was obtained in the sodium methylate reaction at 110-130°C. The results indicated here were of a qualitative nature and no attempt was made to determine the extent of each of the possible reactions. The infra-red data in the region of epoxy absorption (830 cm^{-1}) in the case of the liquid products do not exhibit any appreciable decrease in intensity which would indicate very little side reaction had taken place.

Another possible side reaction which should be considered involves the reaction of resorcinol and γ -aminopropyltriethoxysilane (reaction 9). This product was the only finish in this particular series of compounds that exhibited water miscibility. The solution of this compound is probably succeeded by water hydrolysis to a siloxane type polymer. On the basis of this solubility information it is felt that the compound in question is probably in the following ionized form:



In the case of the product from N,N bis(β -hydroxyethyl)- γ -aminopropyltriethoxysilane (reaction 8) there is no apparent miscibility in water and the hydrolysis product is a polymer. The ionization of the product in this case is probably inhibited by the difference in basicity of these amines and by the fact that the unreacted phenolic hydroxyl can take part in hydrogen bonding with the alcohol groups.

In regard to the reaction of the unsaturated and ester alkoxy silanes with resorcinol we feel that no appreciable side reactions take place under the conditions stated.

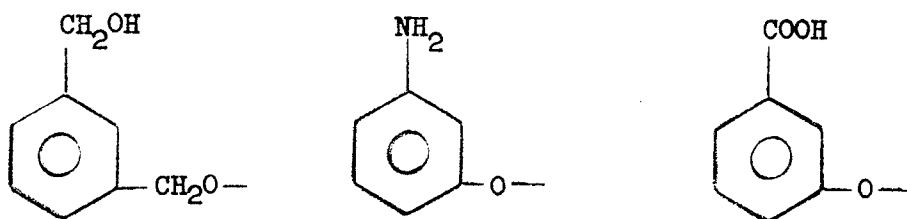
CONCLUSIONS

The preparation of derivatives of NOL-24 via the reaction of resorcinol with alkoxy silanes is a general reaction which can be applied to a variety of starting materials. Derivatives of NOL-24 which contain epoxy, ester, alcoholic, amino and olefin groups have been synthesized using this method. These new finishes are stable compounds that are resistant to hydrolysis by moisture and suitable for commercial application. The performance of these new compounds as finishes will be evaluated in several resin systems and reported on at a later date.

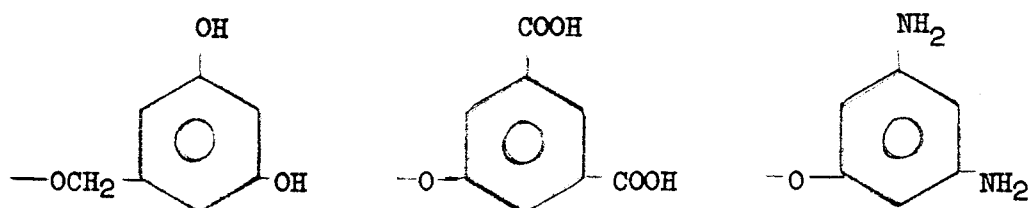
RECOMMENDATIONS

All of the finishes discussed in this report are derived from meta isomer of dihydroxybenzene commonly known as resorcinol. It would also be of value to prepare derivatives of the ortho (pyrocatechol) and para (hydroquinone) isomers and study their properties. Steric effects in the aromatic portion of these molecules could result in modifications in the performance of the finish chemicals and should be studied.

Another area in which effort should be directed is in the preparation of other functional derivatives based on the resorcinol structure. The phenolic hydroxyl could be replaced by other active groups like alcoholic, amine or acid moieties. These groups are known to be very reactive with



epoxy resins for example and should therefore promote stronger bonding between the resin and the finished glass surface. Other polyfunctional derivatives of resorcinol should also be synthesized and evaluated as potential chemical finishes. The following compounds are typical examples:



ACKNOWLEDGEMENT

The author wishes to express his appreciation to Mr. Arthur B. Harris for his able assistance in the experimental portion of this work.

APPENDIX A

EQUIPMENT

A-1. The equipment used to prepare these finishes (Fig. 2) consisted of a 100 ml one-necked flask which was connected with a heated Dean-Stark trap and condenser. Heating was accomplished with a silicone oil bath (Down Corning 550) which was stirred magnetically and could be operated continually at 200°C. The contents of the flask were stirred by a Teflon coated magnet bar. The Dean-Stark trap was heated by means of nichrome wire (0.015") wrapped in asbestos so that the alcohol formed during the course of the reaction could be removed rapidly. The rapid removal of the alcohol insured the proper displacement of the reaction equilibrium and permitted the reaction to proceed at lower temperatures. The volume of alcohol distilled was measured directly in the Dean-Stark trap.

A-2. The Perkin-Elmer model 337 grating infra-red spectrophotometer was used to obtain spectra of the starting silane, the initial reaction mixture and the final reaction product. This instrument is a double beam spectrophotometer with two standard scanning speeds and a total range of 2.5-25 microns ($4000-400\text{ cm}^{-1}$).

APPENDIX B

MATERIALS

B-1. The chemicals used in this study consisted of:

resorcinol - Fisher certified reagent-R17

sodium methylate - Fisher purified-S335

1,3-diaminobenzene (Cl)-General Aniline Dye and Film Co.

m-methoxyphenol - Fisher 223

Epon 828 resin - Shell Chemical Co.

β (3,4-epoxycyclohexyl)ethyltrimethoxysilane (Y4086) - Union Carbide

γ -glycidoxypropyltrimethoxysilane (Y4087) - Union Carbide

N,N bis(β -hydroxyethyl)- γ -aminopropyltriethoxysilane (Y2967) -
Union Carbide

γ -aminopropyltriethoxysilane (A1100) - Union Carbide

β -carbethoxyethyltriethoxysilane (A-1911) - Union Carbide

vinyltriethoxysilane (A151)- Union Carbide

vinyltris(β -methoxyethoxy) silane (A172) - Union Carbide

γ -methacryloxypropyltrimethoxysilane (A174) - Union Carbide

3-cyclohexenetriethoxysilane (Y4407) - Union Carbide

allyltriethoxysilane - Linden Laboratories, Inc.

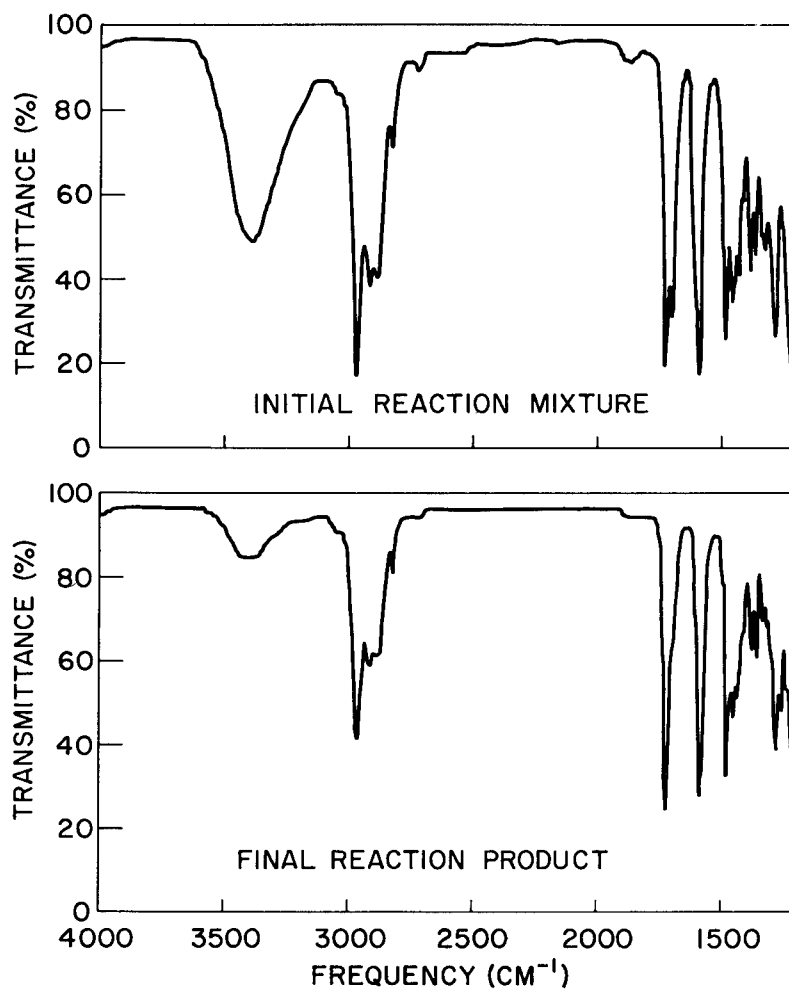


FIG. I m - METHOXYPHENOL- β -CARBETHOXYETHYLTRIETHOXSILANE

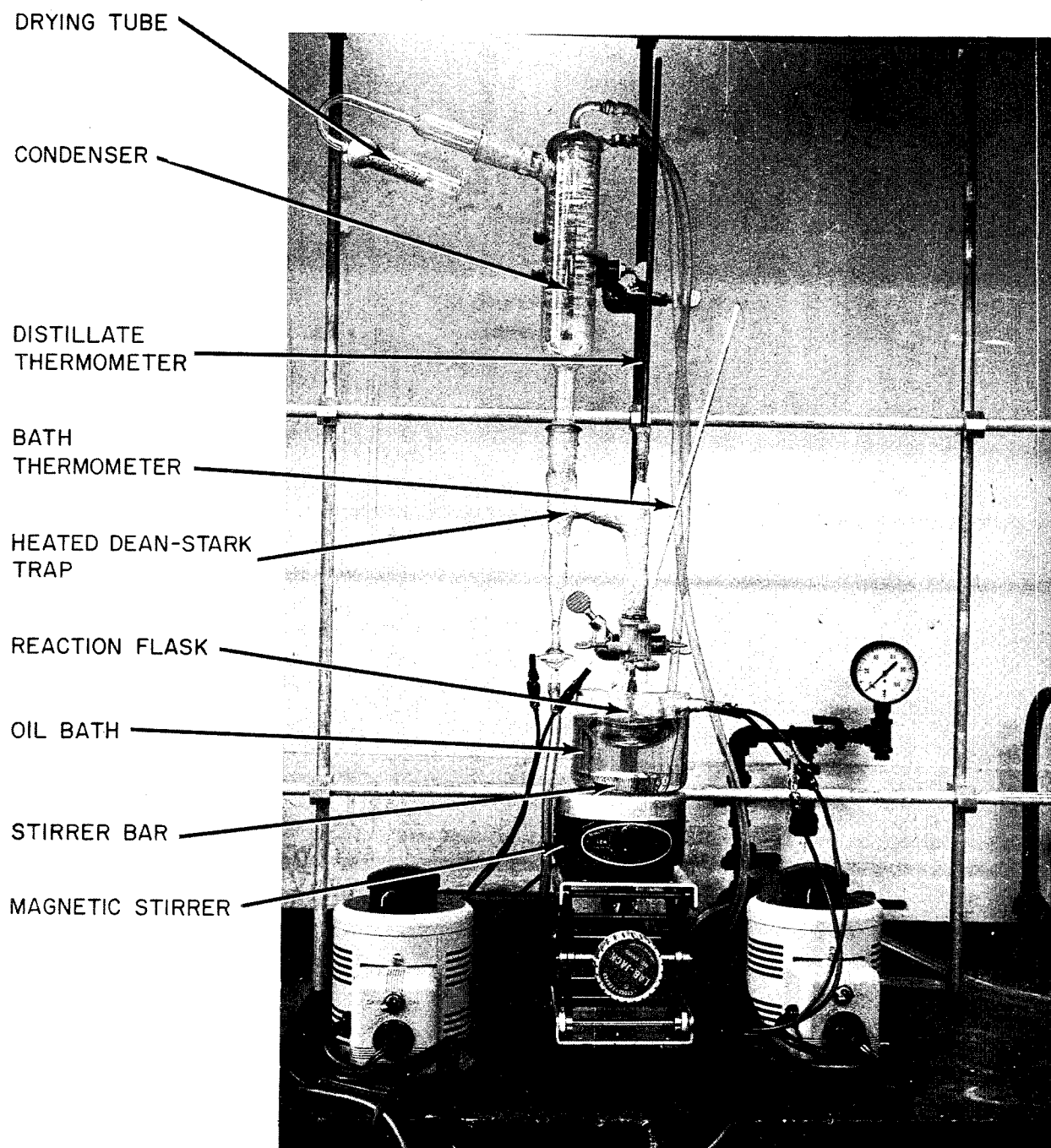


FIG. 2 REACTION EQUIPMENT USED IN THE PREPARATION OF ARYLOXY ALKOXYSILANES

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<p>A total of ten new aryloxy alkoxy silanes have been synthesized that are potential glass fiber finish chemicals for several resin systems. These aryloxysilanes were prepared by the partial condensation reaction between resorcinol and the following silanes: β(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane, N,N bis(β-hydroxyethyl)-γ-aminopropyltriethoxysilane, γ-aminopropyltriethoxysilane, β-carbethoxyethyltriethoxysilane, vinyltriethoxysilane, vinyl-tris(β-methoxyethoxy)silane, γ-methacryloxypropyltrimethoxysilane, 3-cyclohexenetriethoxysilane and allyltriethoxysilane.</p>			

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<p>Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 64-204) NEW ARYLOXY ALKOXYSIANES (I), by James V. Duffy and Porter W. Erickson. 26 Jan. 1965. v.p. charts. NOL task 732/SP-004.</p> <p>UNCLASSIFIED</p> <p>A total of ten new aryloxy alkoxyxilanes have been synthesized that are potential glass fiber finish chemicals for several resin systems. These aryloxyxilanes were prepared by the partial condensation reaction between resorcinol and the following silanes: $\beta(3,4\text{-epoxycyclohexyl})\text{ethyltrimethoxysilane}$, $\gamma\text{-glycidoxypropyltrimethoxysilane}$, $N,N\text{ bis}(\beta\text{-hydroxyethyl})\text{-}\gamma\text{-aminopropyltriethoxysilane}$, $\gamma\text{-aminopropyltriethoxysilane}$, $\beta\text{-carboethoxyethyltriethoxysilane}$, vinyltriethoxysilane, vinyltris($\beta\text{-methoxyethoxy}$)silane, $\gamma\text{-methacryloxypropyltrimethoxysilane}$, 3-cyclohexenetriethoxysilane and allyltriethoxysilane.</p>	<p>1. Finishes - NOL, 24 Glass cloth - Finishes Silanes</p> <p>2. Aryloxy chlorosilane Title Duffy, James V. Erickson, Porter W., jt. author Project</p> <p>Abstract card is unclassified.</p>
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